Inorganic Chemistry

Article

Effect of Branching on the Delayed Fluorescence and Phosphorescence of Simple Borylated Arylamines

Sudhakar Pagidi, Neena K. Kalluvettukuzhy, and Pakkirisamy Thilagar*

Cite This: https://dx.doi.org/10.1021/acs.inorgchem.9b03446



ACCESS	III Metrics & More	E Article Recommendations	s) Supporting Information

ABSTRACT: A donor- π -acceptor strategy is being well exploited in several fields in view of their robust optical properties. However, the impact of branching in quadrupolar $[A-(\pi-D)_2]$ and octupolar $[A-(\pi-D)_3]$ molecules in comparison to parent dipolar $(A-\pi-D)$ molecules on the delayed fluorescence and phosphorescence properties is seldom explored. We have presented herein the distinct and contrasting optical properties of a tridurylborane core bearing $-NH_2$ (1-3) and $-NMe_2$ (4-6) donor moieties, wherein the number of donors is increased systematically. Because of propeller molecular architecture, the donor and acceptor are weakly coupled, and the frontier molecular orbitals are spatially localized. All of the compounds show delayed fluorescence under ambient conditions and persistent phosphorescence at low temperature. Solvent-dependent studies and temperaturedependent luminescence measurements established that quadrupolar (2 and 5) and octupolar (3 and 6) compounds underwent symmetry breaking in the excited state. Curiously, delayed fluorescence and phosphorescence spectra are found to be blue-shifted



and follow the same trend as the fluorescence upon an increase in the branches. The highest quantum yield was observed for dipolar compounds. Besides, the phosphorescence lifetime decreases with an increase in the number of branches. These interesting experimental observations are further supported by quantum-mechanical calculations.

INTRODUCTION

Harnessing the electronic interactions between the electron donors and acceptors is of paramount importance in view of their potential applications in optoelectronics, sensors, and bioimaging.¹⁻³ Electron delocalization is further manipulated by increasing the number of donors or acceptors, thereby generating quadrupolar and octupolar systems. Such compounds find suitable applications in two-photon absorption and solar cells.⁴⁻⁶ It has been established that multipolar compounds show enhanced efficiencies over the parent dipolar systems. Most of the reported multipolar molecules rely on the triphenylamine core with different acceptor units.^{7,8} The effects of branching (arm) in the case of quadrupolar [D-(π -A)₂] and octupolar $[D-(\pi-A)_3]$ molecules on the photophysical properties are investigated in detail.^{4-8,11,15b,c} The more pronounced solvatochromic features of these compounds were explained on the basis of a charge-delocalized/localized intramolecular charge-transfer (ICT) process. In nonpolar solvents, the charge delocalized to all of the arms, whereas in polar solvents, the charge localized on one of the branches, pointing to symmetry breaking in the excited state prior to the emission.^{7,8,17} The effects of branching on the fluorescence emission of various types of compounds are well studied; however, phosphorescence is relatively ill-defined. In recent times, delayed fluorescence materials have gained rapid momentum in view of their potential applications in optoelectronics.9 Numerous publications have boosted our understanding of the thermally activated delayed fluorescence

(TADF) phenomenon.^{9–11} Still, there is a lot of room to understand the delayed fluorescence (DF) in molecules with subtle perturbations in electronic and steric factors, in particular, the branching effects on the DF.

The outstanding optical properties of the π -conjugated boron (B) compounds arise from $p_{\pi}-\pi^*$ conjugation of the vacant p orbital on boron with the π^* orbital of the conjugated π system.¹² Triarylborane (TAB)-containing π -conjugated donor-acceptor systems have been effectively used in organic light-emitting diodes (OLEDs),¹³ nonlinear optics,¹⁴ organic field-effect transistors,¹⁵ fluorescent thermometers,¹⁶ sensors,¹⁷ and bioimaging.¹⁸ TAB compounds with multidimensional ICT properties are of particular interest in view of their promising photophysical properties and robust applica-tions.^{14,18b,c} Even though the chemistry of TAB-based D-A systems is well studied and explored in almost all the fields of materials science and biology, the impact of branching on their photophysical properties, in particular DF and phosphorescence, has seldom been observed.^{11–18} Most of the reported TAB-based multipolar $[D-(\pi-A)_n; n = 1, 2, \text{ or } 3]$ compounds showed a bathochromic shift in the absorption and emission bands with increasing electron-donating strength of the

Received: December 2, 2019



Scheme 1. Synthesis of TDB-Based Molecules 1-6



substituents.¹⁹⁻²¹ However, most of the triphenylamine-based multipolar $[D-(\pi-A)_n; n = 1, 2, \text{ or } 3]$ systems show a blue shift in the absorption and emission spectra with increasing branches/peripheral acceptor units.^{7d} In order to understand such anomalies as well as the effects of branching on the absorption, fluorescence and the unexplored DF and phosphorescence in these multipolar systems with a systematic increase from 1D to 2D to 3D counterparts will be an interesting topic to be studied. Owing to the promising and upcoming applications of TAB in optoelectronics, we have chosen sterically demanding tridurylborane (TDB) as the electron acceptor moiety and simple -NH2 units as donors (1-3). In another series (4-6), the $-NH_2$ donors were replaced with -NMe2 moieties to further see the effect of steric and electronic factors on their optical attributes.^{22a} We found that these compounds exhibit distinct and contrasting optical properties; in particular, the effects of branching on the DF and phosphorescence are prominent. Besides, symmetry breaking in quadrupolar and octupolar compounds is further confirmed by variable-temperature and time-resolved luminescence measurements apart from regular solvent-dependent studies. These interesting optical outcomes are discussed in detail in this Article.

RESULTS AND DISCUSSION

Synthesis and Characterization. Tris(bromoduryl)borane (3a) was synthesized by following the literature procedure reported by Yamaguchi et al., which involves selective monolithiation of 1,4-dibromodurene with nbutyllithium in diethyl ether, followed by quenching with $BF_3 \cdot OEt_2$.¹⁶ Further, selective mono- or dilithiation of **3a** with *n*-butyllithium, followed by quenching with water, yielded 1a and 2a, respectively (Scheme S1). Compounds 1-6 were prepared according to a recently reported procedure.^{22b} The synthesis of 1-3 involves the heating of a mixture of sodium azide, L-proline, copper(I) iodide, and the corresponding pbromo(tridurylborane) derivatives 1a-3a, respectively, at 100 °C in dimethyl sulfoxide (DMSO). Selective para-N,Ndimethylation of 1-3 using sodium hydride and methyl iodide quantitatively yielded 4, 5 and 6, respectively (Scheme 1). All of the compounds are stable under ambient conditions. Compounds 1-6 were characterized by NMR (¹H, ¹³C, and ¹¹B) and high-resolution mass spectrometry (Figures S1-S28). ¹H NMR analysis revealed that compounds 3 and 6 show a simple NMR spectral pattern indicating higher symmetry, while compounds 1, 2, 4, and 5 show a complex pattern pointing to the lower symmetry in a CDCl₃ solution at 25 °C. ¹H NMR spectra of 1, 2, 4, and 5 were recorded in toluene- d_8 at different temperatures between 213 and 323 K (Figure \$29-\$32). The rotation barrier around the B-C bond was

estimated from the temperature-dependent ¹H NMR resonances of compounds in the region 1.80–2.20 ppm (corresponding to the $-CH_3$ groups attached to the duryl moieties). The coalescence temperature (T_c) and free energy of activation $(\Delta G)^{23,24}$ were calculated for 1 ($T_c = 303$ K and $\Delta G = 19$ kcal/mol), 2 ($T_c = 303$ K and $\Delta G = 18.8$ kcal/mol), 4 ($T_c = 303$ K and $\Delta G = 19.5$ kcal/mol), and 5 ($T_c = 313$ K and $\Delta G = 20.5$ kcal/mol). The calculated activation energies of 1, 2, 4, and 5 are in good agreement with the values reported for D–A systems with TAB as the core.^{23,24} Powder X-ray diffraction analysis revealed that the pristine samples of 1, 2, 4, and 5 are amorphous, while 3 and 6 are crystalline in nature (Figure S33).

Article

Molecular Structures. Single crystals of **3** and **6** suitable for X-ray diffraction studies were obtained by the slow evaporation of dichloromethane (DCM) and tetrahydrofuran (THF) solutions, respectively, under ambient conditions (Table S1). Multiple attempts for the crystallization of other compounds under various conditions were unsuccessful. Compound **3** crystallized in triclinic crystal system with $P\overline{1}$ space group and compound **6** in monoclinic crystal system with C2/c space group. In the crystal structure of **6**, the crystallographic C2 axis coincides with the molecular axis along the B1–C13 bond. Compounds **3** and **6** adopt a propeller-like structure in which the boron center possesses a trigonal-planar geometry, with the sum of the C–B–C angle around boron being ~360° (Figure 1). The peripheral nitrogen atoms of the



Figure 1. ORTEP diagrams of the molecular structures of 3 (left) and 6 (right) with thermal ellipsoids drawn at 50% probability. Color code: carbon, gray; nitrogen, blue; boron, pink. All of the hydrogen atoms, except that of the $-NH_2$ unit in 3, are omitted for clarity. The asymmetric unit in the crystal of 3 contains one molecule of 3 and a THF molecule, which is removed for clarity.

amines in both 3 and 6 adopt a pyramidal geometry with sums of the total bond angle of $\sim 357^{\circ}$ and $\sim 351^{\circ}$, respectively. Replacement of the hydrogen atoms with CH₃ groups on the nitrogen atom in 6 induces a little pyramidalization for steric reasons. The dihedral angle between the B–C2 plane and the duryl spacer was found to be in the ranges of 47–59° for 3 and 48–52° for 6, indicating a propellerlike arrangement of the



Figure 2. Absorption (left) and fluorescence emission (right) spectra of 1-6 (solvent = DCM; concentration = $10 \ \mu$ M; $\lambda_{ex} = 370 \ nm$ for 1-3 and 330 nm for 4-6).

three duryl groups. The sterically demanding CH₃ group on the nitrogen leads to elongation of the C(duryl)–N bond in 6 (1.432 Å) compared to that in 3 (1.389 Å). The structural data are in line with the results reported elsewhere by Yamaguchi et al.¹⁹ and Song et al.²⁴ for TDB derivatives.

UV-Vis Absorption and Emission Properties. In the UV-vis absorption spectra, 1 exhibits two clearly separated absorption bands at \sim 321 and \sim 362 nm, while 2 shows a band at \sim 366 nm with an unresolved shoulder peak at \sim 345 nm, whereas a broad absorption band with an absorption maximum at \sim 362 nm is observed for 3. There are no profound changes in the energies of absorption maxima. Only an increase in the molar extinction coefficient (ε) values observed upon an increase in the number of branches in 1-3 reveals their independent behavior (Table S2). Compounds 4-6 exhibited a broad absorption band within the region 300-400 nm (Figure 2). A weak absorption band in the tailing region (360-375 nm) was observed for 4-6 in addition to major broad absorption bands at ~325 nm for 4, ~330 nm for 5, and ~345 nm for 6. Unlike 1-3, the absorption maxima showed a bathochromic shift with increasing numbers of donors in the case of 4-6. Density functional theory (DFT)/time-dependent DFT (TD-DFT) calculations were carried out to understand the nature of electronic transitions involved in the UV-vis absorption features of the compounds, and the major transitions corresponding to the absorption bands are depicted in Table S9. The long-wavelength absorption band of 1 at ~362 nm is assigned to the $S_0 \rightarrow S_1$ (f = 0.1597; $\lambda_{cal.} = 368$ nm) transition, while high-energy band at ~321 nm is assigned to the combined electronic transitions of $S_0 \rightarrow S_2(f = 0.0083;$ $\lambda_{\text{cal.}} = 323 \text{ nm}$) and $S_0 \rightarrow S_3$ (f = 0.0121; $\lambda_{\text{cal.}} = 324 \text{ nm}$). For 2, the absorption band at ~366 nm is attributed to the $S_0 \rightarrow S_1(f)$ = 0.1832; λ_{cal} = 373 nm) electronic transition and the shoulder band at 345 nm closely matches the $S_0 \rightarrow S_2$ (f = 0.0968; $\lambda_{cal.} =$ 354 nm) electronic transition. The broad absorption band for 3 around \sim 362 nm is ascribed to the combined electronic transitions of $S_0 \rightarrow S_1$ (f = 0.1834; $\lambda_{cal} = 373$ nm) and $S_0 \rightarrow S_2$ (f = 0.2016; $\lambda_{cal} = 362$ nm). In the case of **4–6**, the unresolved band in the tailing region of major absorption bands were attributed to $S_0 \rightarrow S_1$ (f = 0.0548; $\lambda_{cal.} = 369$ nm) in the case of 4, $S_0 \rightarrow S_1$ (f = 0.0895; $\lambda_{cal.}$ = 374 nm) and $S_0 \rightarrow S_2$ (f = 0.0217; $\lambda_{\rm cal.}$ = 368 nm) in the case of 5, and S₀ \rightarrow S₁ (f = 0.0912; $\lambda_{cal.} = 377$ nm) and $S_0 \rightarrow S_2$ (f = 0.0787; $\lambda_{cal.} = 373$ nm) in the case of 6. The broad absorption bands in the highenergy region were assigned to electronic transitions such as S₀ \rightarrow S₂ (*f* = 0.0122; $\lambda_{cal.}$ = 334 nm) and S₀ \rightarrow S₃ (*f* = 0.0109; $\lambda_{cal.}$ = 332 nm) for 4 and $S_0 \rightarrow S_3$ (*f* = 0.0097; $\lambda_{cal.}$ = 336 nm) and $S_0 \rightarrow S_4$ (f = 0.0140; $\lambda_{cal} = 336$ nm) for 5, whereas that in the

case of 6 corresponds to the $S_0 \rightarrow S_4$ (f = 0.0114; $\lambda_{cal.} = 339$ nm) transition. The calculated highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gap followed the same trend as that observed in the experimental UV-vis absorption spectra (vide infra). Yamaguchi and co-workers observed a bathochromic shift in absorption and fluorescence emission with increasing number of donors in a series of tris(phenylethynylduryl)borane derivatives, which was explained by the extent of π conjugation.¹⁹ Later in 2006, Lambert et al. compared the optical and electrochemical properties of mono- and tris-(carbazole)-substituted TABs. Charge-transfer (CT) absorption and fluorescence emission of the compounds showed a bathochromic shift with increasing number of carbazole units, attributed to the electronic coupling between the subchromophores of the trimer. Further, the absorption and fluorescence emission spectra showed negative and positive solvatochromism, respectively.²⁰ On the basis of these literature reports and our experimental observations, we tentatively concluded that the bathochromic shift observed in 4-6 with increasing donor units can be attributed to the exciton coupling between the branches.

Solvent-dependent absorption properties of 1-6 were investigated to understand the effect of branching in the ground state by varying the solvent dielectrics (Figure S34 and Table S2). The absorption bands of compounds were sensitive to the changes in solvent polarity, indicating that they originate from the CT transition arising from amine to the boryl unit. For 1-3, the solvatochromic features of CT absorption bands were more profound compared to those of 4-6. Apparently, there seems to be symmetry breaking for quadrupolar (2) and octupolar (3) compounds in the ground state. Very weak intramolecular D-A interactions in 4-6 in the ground state are indicated by their negligible dependence of absorption features upon variation of the solvent polarity.

It is well-known that the $-NH_2$ unit is a weaker electron donor than the $-NMe_2$ unit; hence, one should expect more bathochromic shift for the absorption bands of 4-6 than those of 1-3. Surprisingly, the CT absorption bands of 1-3 showed a bathochromic shift compared to those of 4-6 probably because of the imposed steric repulsions between the methyl groups on nitrogen and the duryl rings in 4-6, which further reduce the electronic coupling between the amines and boron. These results clearly show that not only electronic features but also steric factors are playing a role in controlling their optical properties.³⁰ These observations are in line with the calculated ground-state dipole moments of 1-6 (Table S3).



Figure 3. Temperature-dependent emission spectra of compounds (a) 1 and (b) 4 (solvent = MTHF; concentration = 10 μ M; λ_{ex} = 370 nm for 1 and 330 nm for 4).

Unlike absorption spectra, a structureless broad emission band was observed for 1-6 in a DCM solution upon excitation at their corresponding absorption maxima, which could be attributed to the emission stem from a CT state (Figure 2). With increasing number of donors on the TDB core, a hypsochromic shift in the fluorescence emission spectra was observed in both the $-NH_2$ (1-3) and $-NMe_2$ (4-6) series. Compounds with $-NMe_2$ substituents (4-6) showed a redshifted emission compared to their corresponding -NH₂ derivatives (1-3, respectively), opposite to the trend observed in their UV-vis absorption spectra. Compounds 4-6 showed higher Stokes shifts compared to their corresponding Nunsubstituted 1-3 analogues. A gradual decrease in the Stokes shift was also observed with increasing number of branches in both 1-3 and 4-6. The hypsochromic shift with increasing number of branches due to the repulsive dipole-dipole interactions between branches results in a slight increase of the $S_0 \rightarrow S_1$ energy gap. Compounds 1–6 showed positive solvatofluorochromism with increasing solvent dielectric parameter (Figure S35 and Table S2). The strong solventdependent characteristics of 2, 3, 5, and 6 clearly indicate symmetry breaking in the excited state for quadrupolar and octupolar compounds, giving rise to a dipolar state. The formation of the dipolar CT state is confirmed by the large Stokes shifts and higher exited-state dipole moments compared to that of the ground state (Table S3). To obtain a further understanding of the emissive states, time-resolved fluorescence measurements were carried out in nonpolar (hexane), medium-polar (DCM), and high-polar (DMSO) solvents. The fluorescence lifetime is found to increase with increasing solvent polarity, further confirming that the emissive state possesses CT characteristics (Table S4).

Compounds are brightly emissive in the solid state (Figure S36). Notably, with increasing number of branches, a significant hypsochromic shift was observed in the solid state for both $-NH_2$ and $-NMe_2$ derivatives. Very recently, Yang et al. incorporated mono-, di-, and tris(phenoxazine) (PXZ) donor units into TDB and then exploited them for OLED applications. They observed a red shift in the emission and an increase in the luminescence quantum yield upon an increase in the number of donors in the thin-film state owing to the increased electronic delocalization among the branches.²¹ Compounds 1-6 showed red-shifted fluorescence emission compared to their respective emission in hexane solutions, which can be attributed to the effect of intermolecular

interactions in the solid state. The absolute solid-state quantum efficiencies of 1-6 are found to be 28%, 10%, 8%, 29%, 19%, and 10%, respectively, which shows that the increase of branches elevates the nonradiative decay channels. The above inference was further supported by the gradual increase in the magnitude of nonradiative decay rate constants with increasing number of branches in both the 1-3 and 4-6 series (Table S5).

Temperature-Dependent Luminescence. In order to further confirm the symmetry breaking at the excited state and the formation of the dipolar charge-transfer state, we carried out temperature-dependent (298-77 K) steady-state luminescence measurements for 1-6 in a 2-methyltetrahydrofuran (MTHF) solution (Figures 3 and S37 and 38) because the charge-transfer state is sensitive to the environment. Compound 1 showed a structureless broad emission band (fwhm = \sim 96 nm) at \sim 520 nm in a MTHF solution at 298 K $(\lambda_{ex} = 370 \text{ nm})$. As the temperature decreased from 298 to 140 K, a gradual red shift of \sim 32 nm was observed. This can be attributed to an increase in the solvent dielectric constant and thus stabilization of the CT state. Cooling to the glass transition temperature of MTHF (~95 K) resulted in a blue shift of the emission, ascribed to the slight increase of the solvent relaxation time.^{25,26} A further cooling (<95 K) showed a pronounced blue-shifted emission ($\lambda_{em} = 462 \text{ nm}$), and no significant changes in the emission spectra could be seen even after cooling to 77 K. Notably, the emission ($\lambda_{em} = 462 \text{ nm}$) at 77 K is comparable to the emissions in the nonpolar toluene solvent ($\lambda_{em} = 467 \text{ nm}$) and solid state ($\lambda_{em} = 470 \text{ nm}$). This is due to the fact that the fluorescence time scales are much faster than the solvent relaxation times in the nonpolar frozen glassy matrix of MTHF below 95 K. 25,26 Interestingly, we could see a broad emission band (fwhm = ~ 65 nm) even at 77 K, indicating CT characteristics of the emissive state in the frozen nonpolar matrix.

Under similar experimental conditions, the temperaturedependent luminescence spectral features of 2-6 are the same as that of 1, except in the frozen matrix (Figures 3 and S37 and S38). Below 95 K, three emission peaks were observed for 2 and 3, while there were two emission bands for 5 and 6 in MTHF, which are attributed to the combination of fluorescence and phosphorescence emissions in the steady state (Figure S37). For compounds 2 and 3, the phosphorescence spectra appear to be slightly vibronic in structure with an average spacing of ca. 1200 cm⁻¹; similar kinds of spectral pubs.acs.org/IC



Figure 4. Prompt and delayed emission spectra of compounds (a) **1** and (b) **4** at 77 and 298 K (solvent = MTHF; concentration = $10 \ \mu$ M; λ_{ex} = 370 nm for **1** and 330 nm for **4**). The insets show phosphorescence emissions of compounds under UV-light illumination.



Figure 5. Phosphorescence spectra of compounds (a) 1–3 and (b) 4–6 at 77 K in the solid state (λ_{ex} = 370 nm for 1 and 330 nm for 4).

features were also observed by Marder et al. for [4-(tert-butyl)phenyl]bis(fluoromesityl)borane below 95 K in MTHF.²⁶ The temperature-dependent luminescence measurements undoubtedly revealed that the dipolar nature of the excited states of quadrupolar (2 and 5) and octupolar (3 and 6) compounds support symmetry breaking at the excited state.

Both steady-state and time-resolved emission measurements were carried out at 298 and 77 K to probe their fluorescence, phosphorescence, and DF characteristics in both solution and thin-film states for all compounds (Figures 4 and S39 and Table S6). In the case of compound 1, the emission is located at ~462 nm with a lifetime (τ) of ~13.4 ns can be ascribed to fluorescence (prompt fluorescence) at 77 K. The corresponding delayed component was around \sim 503 nm with τ = ~957.74 ms; such a red-shifted and long-lived emission compared to prompt fluorescence could be phosphorescence. At 298 K, the prompt ($\tau = \sim 12.86$ ns) and delayed ($\tau = \sim 5.14$ μ s) emission spectra were the same with maxima around ~520 nm. Compounds 2-6 also showed similar kinds of emission feature at 298 and 77 K. Notably, a gradual increase in the emission intensity can be noted when the temperature increases from 250 to 298 K in compounds 4-6 (Figure S40), presumably due to the contribution of DF.⁹ The calculated singlet and triplet splitting energy (ΔE_{sT} ; determined from the peak position) values lie in the range of 0.15-0.29 eV, indicating that TADF might be in operation, thus the increase in the emission intensity with an increase in the temperature for compounds 4-6; however, for 1-3, a decrease in the emission intensity can be noted even when the $\Delta E_{\rm ST}$ values were in the range 0.21–0.27 eV, pointing to the elevation of the nonradiative channels with increasing temperature (Figure S40 and Table S8).³¹ The phosphorescence lifetime decreases with increasing number of branches at 77 K (Table S6). For instance, compound 1 ($\tau = \sim 957.74$ ms) showed a longer-lived lifetime than 2 ($\tau = \sim 666.24$ ms) and 3 ($\tau = \sim 494.45$ ms). A similar observation was noted for 4 ($\tau = 928.00$ ms), 5 ($\tau = 795.23$ ms), and 6 ($\tau = 665.50$ ms) as well. Involvement of triplets in DF is further supported by the decrease of DF under oxygen-aerated MTHF solutions (Figure S41).

Further, the prompt and delayed emission spectra and decay profiles were collected at 298 and 77 K in the thin-film state (Figures S42 and S43 and Table S7). In the case of 1, prompt fluorescence was observed at 478 nm ($\tau = 8.07$ ns), while phosphorescence was located at 517 nm (τ = 329.33 ms) at 77 K. Compounds 2-6 also showed phosphorescence characteristics with millisecond lifetime at 77 K. Further, to confirm the phosphorescence emission characteristics, time-resolved decay profiles of 4 at different temperatures were collected as representative examples. An increase in the excited-state lifetime upon decreasing temperature further supports the phosphorescence nature of the emission (Figure S43). It is worth mentioning that phosphorescence of TABs at 77 K with different lifetimes was reported independently by Marder et al.,²⁶ Yamguchi et al.,²⁷ Wagner et al.,²⁸ and Wang et al.²⁹ Remarkably, the phosphorescence spectra, like fluorescence, are blue-shifted with increasing number of branches (Figure 5). Compounds also showed DF with microsecond lifetime at



Figure 6. Frontier molecular orbitals (HOMO and LUMO) and their associated energies for compounds 1-6 (energies are not up to the scale).

298 K in the solid state and followed the same trend as that of phosphorescence and fluorescence, i.e., hypsochromic shift with increasing number of branches in the series 1-3 and 4-6(Figure S42). The involvement of triplet states in the emission features of the compounds was confirmed by measuring the delayed emission and delayed emission decay profiles under an oxygen atmosphere at 298 K. Compounds 1-6 showed a significant quenching of the luminescence intensity and excited-state lifetime in the presence of oxygen (Figures S45 and S46). Further, a decrease in the emission quantum yields (from 28% to 25% for 1, from 10% to 9% for 2, from 8% to 6% for 3, from 29% to 27% for 4, from 19% to 16% for 5, and from 10% to 7% for 6) was observed in the presence of oxygen. Upon an increase in the donor strength from $-NH_2$ to -NMe₂, the triplet energy levels did not perturb much; however, the singlet energy levels were significantly destabilized and showed blue-shifted fluorescence at 77 K (Figures 5 and S47 and Table S8).

Theoretical Modeling. To further obtain insight into the electronic structure and photophysical properties, theoretical calculations were performed using a DFT/B3LYP/6-31G(d) approach.³² Vertical transition energies were estimated on ground-state-optimized geometries using the TD-DFT methodology (Table S9). The molecular orbital coefficients of the HOMOs for 1-3 reside on the NH₂ units with large contribution from the amine-attached duryl moieties (Figure 6). The HOMO level is slightly destabilized with increasing number of donors. The orbital coefficients of the LUMOs for 1-3 are delocalized over the entire molecule, with significantly large contribution from the boron atom. Notably, the LUMO level was destabilized with an increment of ~0.17 eV per each amine incorporation; however, no such type of trend was observed for the HOMO levels for compounds 1-3. On the other hand, the frontier molecular orbital distribution patterns in 4-6 are different. For 4 and 5, the HOMOs are localized on the amine units with a slight contribution from the duryl moieties attached to amines. In contrast, the HOMO is exclusively localized on one of the NMe2 groups, with some contribution from its attached duryl ring; there is a minor contribution from the other NMe_2 groups in 6. The LUMOs are delocalized over the entire molecule except on the amines. The increase in the number of donors has a negligible effect on the LUMO energy levels. The extent of frontier molecular orbital destabilization in 4-6 is less compared to that in 1-3with increasing donors. The energy gap in 4-6 is slightly lower

than that in 1-3, which is in good agreement with the experimental observations.

Remarkably, the LUMO level for **4–6** is more stabilized than that of the **1–3** series, indicating the stronger electronaccepting properties of boron as a result of weak/negligible electronic interaction between the amine and boron in the ground state, which is well illustrated by their insignificant absorption solvatochromic characteristics. The estimated difference in vertical transition energies between the singlet (S₁) and triplet (T₁) excited states is in the range of 0.3–0.6 eV, supporting the trend of $\Delta E_{\rm ST}$ determined from the experiments (Tables S8 and S9).

CONCLUSIONS

In conclusion, the design, synthesis, and intriguing optical properties of a series of TDB-based dipolar (1 and 4), quadrupolar (2 and 5), and octupolar (3 and 6) compounds were reported. The degree of CT and energy of the CT states were fine-tuned by systematically varying the number and strength of the donors as well as the symmetry of the molecular systems. Because of the propeller molecular architecture, the donor and acceptor are weakly coupled, and the frontier molecular orbitals are specially localized. These arrangements lowered the energy gap between the S_1 and T_1 excited states and facilitated reverse intersystem crossing in compounds 1-6. Thus, all of the compounds show DF under ambient conditions and persistent phosphorescence at low temperature. The DF and phosphorescence emissions were gradually blueshifted with an increase in the number of donor branches. The detailed optical and computational studies on these compounds established that symmetry breaking in the excited state is responsible for the observed intriguing optical properties. Of all of the compounds, the dipolar molecules 1 and 4 exhibited the highest solid-state quantum yields. To the best of our knowledge, these are the simplest boron-based donoracceptor molecules showing DF and persistent phosphorescence.

ASSOCIATED CONTENT

9 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03446.

Synthesis and characterization details, crystallographic structural refinement data, and supporting optical

characterization details and DFT calculation results (PDF) $% \left(PDF\right) =\left(PDF\right) \left(PDF\right) \left($

Accession Codes

CCDC 993251 and 993252 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Pakkirisamy Thilagar – Department of Inorganic and Physical Chemistry, Indian Institute of Science (IISc), Bangalore 560012, India; ◎ orcid.org/0000-0001-9569-7733; Email: thilagar@iisc.ac.in

Authors

- Sudhakar Pagidi Department of Inorganic and Physical Chemistry, Indian Institute of Science (IISc), Bangalore 560012, India
- **Neena K. Kalluvettukuzhy** Department of Inorganic and Physical Chemistry, Indian Institute of Science (IISc), Bangalore 560012, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.9b03446

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

P.T. thanks the Science and Engineering Research Board (SERB), New Delhi, India, and IISc for financial support. S.P. and N.K.K. thank the SERB, New Delhi, India, for financial support.

REFERENCES

(1) (a) Duan, L.; Qiao, J.; Sun, Y.; Qiu, Y. Strategies to Design Bipolar Small Molecules for OLEDs: Donor-Acceptor Structure and Non-Donor-Acceptor Structure. Adv. Mater. 2011, 23 (9), 1137-1144. (b) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly efficient organic light-emitting diodes from delayed fluorescence. Nature 2012, 492 (7428), 234-238. (c) Xu, L.; Zhu, H.; Long, G.; Zhao, J.; Li, D.; Ganguly, R.; Li, Y.; Xu, Q.-H.; Zhang, Q. 4-Diphenylamino-phenyl substituted pyrazine: nonlinear optical switching by protonation. J. Mater. Chem. C 2015, 3 (35), 9191-9196. (d) Cao, X.; Zhang, D.; Zhang, S.; Tao, Y.; Huang, W. CN-Containing donor-acceptor-type small-molecule materials for thermally activated delayed fluorescence OLEDs. J. Mater. Chem. C 2017, 5 (31), 7699-7714. (e) Olivier, Y.; Moral, M.; Muccioli, L.; Sancho-García, J.-C. Dynamic nature of excited states of donor-acceptor TADF materials for OLEDs: how theory can reveal structure-property relationships. J. Mater. Chem. C 2017, 5 (23), 5718-5729. (f) Ryu, J. Y.; Lee, J. M.; Van Nghia, N.; Lee, K. M.; Lee, S.; Lee, M. H.; Stang, P. J.; Lee, J. Supramolecular Pt(II) and Ru(II) Trigonal Prismatic Cages Constructed with a Tris(pyridyl)borane Donor. Inorg. Chem. 2018, 57 (18), 11696-11703. (g) Tang, M.-C.; Lee, C.-H.; Ng, M.; Wong, Y.-C.; Chan, M.-Y.; Yam, V. W.-W. Highly Emissive Fused Heterocyclic Alkynylgold(III) Complexes for Multiple Color Emission Spanning from Green to Red for Solution-Processable Organic Light-Emitting Devices. *Angew. Chem., Int. Ed.* **2018**, *57* (19), 5463–5466. (h) Lee, C.-H.; Tang, M.-C.; Cheung, W.-L.; Lai, S.-L.; Chan, M.-Y.; Yam, V. W.-W. Highly luminescent phosphine oxidecontaining bipolar alkynylgold(iii) complexes for solution-processable organic light-emitting devices with small efficiency roll-offs. *Chem. Sci.* **2018**, 9 (29), 6228–6232.

(2) (a) Jin, S.; Furukawa, K.; Addicoat, M.; Chen, L.; Takahashi, S.; Irle, S.; Nakamura, T.; Jiang, D. Large pore donor-acceptor covalent organic frameworks. Chem. Sci. 2013, 4 (12), 4505-4511. (b) Zhang, J.; Chen, W.; Kalytchuk, S.; Li, K. F.; Chen, R.; Adachi, C.; Chen, Z.; Rogach, A. L.; Zhu, G.; Yu, P. K. N.; Zhang, W.; Cheah, K. W.; Zhang, X.; Lee, C.-S. Self-Assembly of Electron Donor-Acceptor-Based Carbazole Derivatives: Novel Fluorescent Organic Nanoprobes for Both One- and Two-Photon Cellular Imaging. ACS Appl. Mater. Interfaces 2016, 8 (18), 11355-11365. (c) Schäfer, J.; Holzapfel, M.; Schmiedel, A.; Steiner, U. E.; Lambert, C. Fine tuning of electron transfer and spin chemistry parameters in triarylamine-bridgenaphthalene diimide dyads by bridge substituents. Phys. Chem. Chem. Phys. 2018, 20 (42), 27093-27104. (d) Pachfule, P.; Acharjya, A.; Roeser, J.; Sivasankaran, R. P.; Ye, M.-Y.; Brückner, A.; Schmidt, J.; Thomas, A. Donor-acceptor covalent organic frameworks for visible light induced free radical polymerization. Chem. Sci. 2019, 10 (36), 8316-8322. (e) He, J.; Rauch, F.; Friedrich, A.; Sieh, D.; Ribbeck, T.; Krummenacher, I.; Braunschweig, H.; Finze, M.; Marder, T. B. N-Heterocyclic Olefins as Electron Donors in Combination with Triarylborane Acceptors: Synthesis, Optical and Electronic Properties of D-π-A Compounds. Chem. - Eur. J. 2019, 25 (60), 13777-13784. (f) Kunchala, D.; Sa, S.; Navak, P.; Ponniah S, J.; Venkatasubbaiah, K. Tetrahydrodibenzophenanthridine-Based Boron-Bridged Polycyclic Aromatic Hydrocarbons: Synthesis, Structural Diversity, and Optical Properties. Organometallics 2019, 38 (4), 870-878.

(3) (a) Parab, K.; Venkatasubbaiah, K.; Jäkle, F. Luminescent Triarylborane-Functionalized Polystyrene: Synthesis, Photophysical Characterization, and Anion-Binding Studies. J. Am. Chem. Soc. 2006, 128 (39), 12879–12885. (b) Xu, B.; Wu, X.; Li, H.; Tong, H.; Wang, L. Selective Detection of TNT and Picric Acid by Conjugated Polymer Film Sensors with Donor-Acceptor Architecture. Macromolecules 2011, 44 (13), 5089–5092. (c) Dhanunjayarao, K.; Mukundam, V.; Venkatasubbaiah, K. Tetracoordinate Imidazole-Based Boron Complexes for the Selective Detection of Picric Acid. Inorg. Chem. 2016, 55 (21), 11153–11159. (d) Narayanaswamy, K.; Yadagiri, B.; Chowdhury, T. H.; Swetha, T.; Islam, A.; Gupta, V.; Singh, S. P. Impact of A-D-A-Structured Dithienosilole- and Phenoxazine-Based Small Molecular Material for Bulk Heterojunction and Dopant-Free Perovskite Solar Cells. Chem. - Eur. J. 2019, 25, 16320.

(4) (a) Terenziani, F.; Le Droumaguet, C.; Katan, C.; Mongin, O.; Blanchard-Desce, M. Effect of Branching on Two-Photon Absorption in Triphenylbenzene Derivatives. ChemPhysChem 2007, 8 (5), 723-734. (b) Makarov, N. S.; Mukhopadhyay, S.; Yesudas, K.; Brédas, J.-L.; Perry, J. W.; Pron, A.; Kivala, M.; Müllen, K. Impact of Electronic Coupling, Symmetry, and Planarization on One- and Two-Photon Properties of Triarylamines with One, Two, or Three Diarylboryl Acceptors. J. Phys. Chem. A 2012, 116 (15), 3781-3793. (c) Poronik, Y. M.; Hugues, V.; Blanchard-Desce, M.; Gryko, D. T. Octupolar Merocyanine Dyes: A New Class of Nonlinear Optical Chromophores. Chem. - Eur. J. 2012, 18 (30), 9258-9266. (d) Yan, L.; Chen, X.; He, Q.; Wang, Y.; Wang, X.; Guo, Q.; Bai, F.; Xia, A.; Aumiler, D.; Vdović, S.; Lin, S. Localized Emitting State and Energy Transfer Properties of Quadrupolar Chromophores and (Multi)Branched Derivatives. J. Phys. Chem. A 2012, 116 (34), 8693-8705. (e) Wang, Y.; Yin, S.; Liu, J.; Yao, L.; Wang, G.; Liu, D.; Jing, B.; Cheng, L.; Zhong, H.; Shi, X.; Fang, Q.; Qian, S. Probing ultrafast excited state dynamics and nonlinear absorption properties of three star-shaped conjugated oligomers with 1,3,5-triazine core. RSC Adv. 2014, 4 (21), 10960-10967.

(5) (a) Roquet, S.; Cravino, A.; Leriche, P.; Alévêque, O.; Frère, P.; Roncali, J. Triphenylamine-Thienylenevinylene Hybrid Systems with Internal Charge Transfer as Donor Materials for Heterojunction Solar Cells. J. Am. Chem. Soc. 2006, 128 (10), 3459-3466. (b) He, G. S.; Tan, L.-S.; Zheng, Q.; Prasad, P. N. Multiphoton Absorbing Materials: Molecular Designs, Characterizations, and Applications. Chem. Rev. 2008, 108 (4), 1245-1330. (c) Kim, H. M.; Sik Seo, M.; Jeon, S.-J.; Rae Cho, B. Two-photon absorption properties of hexasubstituted benzene derivatives. Comparison between dipolar and octupolar molecules. Chem. Commun. 2009, No. 47, 7422-7424. (d) Sissa, C.; Manna, A. K.; Terenziani, F.; Painelli, A.; Pati, S. K. Beyond the Förster formulation for resonance energy transfer: the role of dark states. Phys. Chem. Chem. Phys. 2011, 13 (28), 12734-12744. (e) Ongungal, R. M.; Sivadas, A. P.; Kumar, N. S. S.; Menon, S.; Das, S. Self-assembly and mechanochromic luminescence switching of trifluoromethyl substituted 1,3,4-oxadiazole derivatives. J. Mater. Chem. C 2016, 4 (40), 9588-9597.

(6) (a) Walker, B.; Kim, C.; Nguyen, T.-Q. Small Molecule Solution-Processed Bulk Heterojunction Solar Cells. *Chem. Mater.* **2011**, 23 (3), 470–482. (b) Zhang, J.; Yu, J.; He, C.; Deng, D.; Zhang, Z.-G.; Zhang, M.; Li, Z.; Li, Y. Solution-processable star-shaped photovoltaic organic molecules based on triphenylamine and benzothiadiazole with longer pi-bridge. *Org. Electron.* **2012**, *13* (1), 166–172. (c) Kengthanomma, T.; Thamyongkit, P.; Gasiorowski, J.; Ramil, A. M.; Sariciftci, N. S. On the potential of porphyrin-spiked triarylamine stars for bulk heterojunction solar cells. *J. Mater. Chem. A* **2013**, *1* (35), 10524–10531.

(7) (a) Porrès, L.; Mongin, O.; Katan, C.; Charlot, M.; Pons, T.; Mertz, J.; Blanchard-Desce, M. Enhanced Two-Photon Absorption with Novel Octupolar Propeller-Shaped Fluorophores Derived from Triphenylamine. Org. Lett. 2004, 6 (1), 47-50. (b) Easwaramoorthi, S.; Thamaraiselvi, P.; Duraimurugan, K.; Beneto, A. J.; Siva, A.; Nair, B. U. Charge instability of symmetry broken dipolar states in quadrupolar and octupolar triphenylamine derivatives. Chem. Commun. 2014, 50 (52), 6902-6905. (c) Cvejn, D.; Michail, E.; Polyzos, I.; Almonasy, N.; Pytela, O.; Klikar, M.; Mikysek, T.; Giannetas, V.; Fakis, M.; Bureš, F. Modulation of (non)linear optical properties in tripodal molecules by variation of the peripheral cyano acceptor moieties and the π -spacer. J. Mater. Chem. C 2015, 3 (28), 7345-7355. (d) Cvejn, D.; Michail, E.; Seintis, K.; Klikar, M.; Pytela, O.; Mikysek, T.; Almonasy, N.; Ludwig, M.; Giannetas, V.; Fakis, M.; Bureš, F. Solvent and branching effect on the two-photon absorption properties of push-pull triphenylamine derivatives. RSC Adv. 2016, 6 (16), 12819-12828.

(8) (a) Parthasarathy, V.; Fery-Forgues, S.; Campioli, E.; Recher, G.; Terenziani, F.; Blanchard-Desce, M. Dipolar versus Octupolar Triphenylamine-Based Fluorescent Organic Nanoparticles as Brilliant One- and Two-Photon Emitters for (Bio)imaging. *Small* **2011**, 7 (22), 3219–3229. (b) Cvejn, D.; Achelle, S.; Pytela, O.; Malval, J.-P.; Spangenberg, A.; Cabon, N.; Bureš, F.; Robin-le Guen, F. Tripodal molecules with triphenylamine core, diazine peripheral groups and extended π -conjugated linkers. *Dyes Pigm.* **2016**, *124*, 101–109.

(9) (a) Tao, Y.; Yuan, K.; Chen, T.; Xu, P.; Li, H.; Chen, R.; Zheng, C.; Zhang, L.; Huang, W. Thermally Activated Delayed Fluorescence Materials Towards the Breakthrough of Organoelectronics. Adv. Mater. 2014, 26 (47), 7931-7958. (b) Godumala, M.; Choi, S.; Cho, M. J.; Choi, D. H. Thermally activated delayed fluorescence blue dopants and hosts: from the design strategy to organic light-emitting diode applications. J. Mater. Chem. C 2016, 4 (48), 11355-11381. (c) Yang, Z.; Mao, Z.; Xie, Z.; Zhang, Y.; Liu, S.; Zhao, J.; Xu, J.; Chi, Z.; Aldred, M. P. Recent advances in organic thermally activated delayed fluorescence materials. Chem. Soc. Rev. 2017, 46 (3), 915-1016. (d) Furue, R.; Matsuo, K.; Ashikari, Y.; Ooka, H.; Amanokura, N.; Yasuda, T. Highly Efficient Red-Orange Delayed Fluorescence Emitters Based on Strong π -Accepting Dibenzophenazine and Dibenzoquinoxaline Cores: toward a Rational Pure-Red OLED Design. Adv. Opt. Mater. 2018, 6 (5), 1701147. (e) Cai, X.; Su, S.-J. Marching Toward Highly Efficient, Pure-Blue, and Stable Thermally Activated Delayed Fluorescent Organic Light-Emitting Diodes. Adv. Funct. Mater. 2018, 28 (43), 1802558.

(10) (a) Numata, M.; Yasuda, T.; Adachi, C. High efficiency pure blue thermally activated delayed fluorescence molecules having 10Hphenoxaborin and acridan units. Chem. Commun. 2015, 51 (46), 9443–9446. (b) Suzuki, K.; Kubo, S.; Shizu, K.; Fukushima, T.; Wakamiya, A.; Murata, Y.; Adachi, C.; Kaji, H. Triarylboron-Based Fluorescent Organic Light-Emitting Diodes with External Quantum Efficiencies Exceeding 20%. Angew. Chem., Int. Ed. 2015, 54 (50), 15231-15235. (c) Hatakeyama, T.; Shiren, K.; Nakajima, K.; Nomura, S.; Nakatsuka, S.; Kinoshita, K.; Ni, J.; Ono, Y.; Ikuta, T. Ultrapure Blue Thermally Activated Delayed Fluorescence Molecules: Efficient HOMO-LUMO Separation by the Multiple Resonance Effect. Adv. Mater. 2016, 28 (14), 2777-2781. (d) Wu, T.-L.; Huang, M.-J.; Lin, C.-C.; Huang, P.-Y.; Chou, T.-Y.; Chen-Cheng, R.-W.; Lin, H.-W.; Liu, R.-S.; Cheng, C.-H. Diboron compound-based organic light-emitting diodes with high efficiency and reduced efficiency rolloff. Nat. Photonics 2018, 12 (4), 235-240.

(11) (a) Wang, S.; Yang, D.-T.; Lu, J.; Shimogawa, H.; Gong, S.; Wang, X.; Mellerup, S. K.; Wakamiya, A.; Chang, Y.-L.; Yang, C.; Lu, Z.-H. In Situ Solid-State Generation of (BN)2-Pyrenes and Electroluminescent Devices. Angew. Chem., Int. Ed. 2015, 54 (50), 15074-15078. (b) Kitamoto, Y.; Namikawa, T.; Ikemizu, D.; Miyata, Y.; Suzuki, T.; Kita, H.; Sato, T.; Oi, S. Light blue and green thermally activated delayed fluorescence from 10H-phenoxaborin-derivatives and their application to organic light-emitting diodes. J. Mater. Chem. C 2015, 3 (35), 9122-9130. (c) Chen, D.-G.; Lin, T.-C.; Chen, C.-L.; Chen, Y.-T.; Chen, Y.-A.; Lee, G.-H.; Chou, P.-T.; Liao, C.-W.; Chiu, P.-C.; Chang, C.-H.; Lien, Y.-J.; Chi, Y. Optically Triggered Planarization of Boryl-Substituted Phenoxazine: Another Horizon of TADF Molecules and High-Performance OLEDs. ACS Appl. Mater. Interfaces 2018, 10 (15), 12886-12896. (d) Neena, K. K.; Sudhakar, P.; Thilagar, P. Catalyst- and Template-Free Ultrafast Visible-Light-Triggered Dimerization of Vinylpyridine-Functionalized Tetraarylaminoborane: Intriguing Deep-Blue Delayed Fluorescence. Angew. Chem., Int. Ed. 2018, 57 (51), 16806-16810. (e) Gao, Y.; Pan, Q.-Q.; Zhao, L.; Geng, Y.; Su, T.; Gao, T.; Su, Z.-M. Realizing performance improvement of blue thermally activated delayed fluorescence molecule DABNA by introducing substituents on the para-position of boron atom. Chem. Phys. Lett. 2018, 701, 98-102.

(12) (a) Doty, J. C.; Babb, B.; Grisdale, P. J.; Glogowski, M.; Williams, J. L. R. Boron photochemistry: IX. Synthesis and fluorescent properties of dimesityl-phenylboranes. J. Organomet. Chem. 1972, 38 (2), 229-236. (b) Proń, A.; Baumgarten, M.; Müllen, K. Phenylene Bridged Boron-Nitrogen Containing Dendrimers. Org. Lett. 2010, 12 (19), 4236-4239. (c) Hudnall, T. W.; Chiu, C.-W.; Gabbaï, F. P. Fluoride Ion Recognition by Chelating and Cationic Boranes. Acc. Chem. Res. 2009, 42 (2), 388-397. (d) Mukherjee, S.; Thilagar, P. Stimuli and shape responsive 'boron-containing' luminescent organic materials. J. Mater. Chem. C 2016, 4 (14), 2647-2662. (e) Ren, Y.; Jäkle, F. Merging thiophene with boron: new building blocks for conjugated materials. Dalton Trans. 2016, 45 (36), 13996-14007. (f) Ji, L.; Griesbeck, S.; Marder, T. B. Recent developments in and perspectives on three-coordinate boron materials: a bright future. Chem. Sci. 2017, 8 (2), 846–863. (g) Li, S.-Y.; Sun, Z.-B.; Zhao, C.-H. Charge-Transfer Emitting Triarylborane π -Electron Systems. Inorg. Chem. 2017, 56 (15), 8705-8717. (h) Mellerup, S. K.; Wang, S. Boron-based stimuli responsive materials. Chem. Soc. Rev. 2019, 48 (13), 3537-3549.

(13) (a) Lee, Y. H.; Park, S.; Oh, J.; Shin, J. W.; Jung, J.; Yoo, S.; Lee, M. H. Rigidity-Induced Delayed Fluorescence by Ortho Donor-Appended Triarylboron Compounds: Record-High Efficiency in Pure Blue Fluorescent Organic Light-Emitting Diodes. ACS Appl. Mater. Interfaces 2017, 9 (28), 24035–24042. (b) Turkoglu, G.; Cinar, M. E.; Ozturk, T. Triarylborane-Based Materials for OLED Applications. Molecules 2017, 22 (9), 1522. (c) Matsui, K.; Oda, S.; Yoshiura, K.; Nakajima, K.; Yasuda, N.; Hatakeyama, T. One-Shot Multiple Borylation toward BN-Doped Nanographenes. J. Am. Chem. Soc. 2018, 140 (4), 1195–1198. (d) Brend'amour, S.; Gilmer, J.; Bolte,

(14) (a) Yuan, Z.; Collings, J. C.; Taylor, N. J.; Marder, T. B.; Jardin, C.; Halet, J.-F. Linear and Nonlinear Optical Properties of Three-Coordinate Organoboron Compounds. J. Solid State Chem. 2000, 154 (1), 5-12. (b) Yuan, Z.; Entwistle, C. D.; Collings, J. C.; Albesa-Jové, D.; Batsanov, A. S.; Howard, J. A. K.; Taylor, N. J.; Kaiser, H. M.; Kaufmann, D. E.; Poon, S.-Y.; Wong, W.-Y.; Jardin, C.; Fathallah, S.; Boucekkine, A.; Halet, J.-F.; Marder, T. B. Synthesis, Crystal Structures, Linear and Nonlinear Optical Properties, and Theoretical Studies of (p-R-Phenyl)-, (p-R-Phenylethynyl)-, and (E)-[2-(p-R-Phenyl)ethenyl]dimesitylboranes and Related Compounds. Chem. -Eur. J. 2006, 12 (10), 2758-2771. (c) Griesbeck, S.; Michail, E.; Rauch, F.; Ogasawara, H.; Wang, C.; Sato, Y.; Edkins, R. M.; Zhang, Z.; Taki, M.; Lambert, C.; Yamaguchi, S.; Marder, T. B. The Effect of Branching on the One- and Two-Photon Absorption, Cell Viability, and Localization of Cationic Triarylborane Chromophores with Dipolar versus Octupolar Charge Distributions for Cellular Imaging. Chem. - Eur. J. 2019, 25 (57), 13164-13175. (d) Griesbeck, S.; Michail, E.; Wang, C.; Ogasawara, H.; Lorenzen, S.; Gerstner, L.; Zang, T.; Nitsch, J.; Sato, Y.; Bertermann, R.; Taki, M.; Lambert, C.; Yamaguchi, S.; Marder, T. B. Tuning the π -bridge of quadrupolar triarylborane chromophores for one- and two-photon excited fluorescence imaging of lysosomes in live cells. Chem. Sci. 2019, 10 (20), 5405-5422.

(15) (a) Hatakeyama, T.; Hashimoto, S.; Seki, S.; Nakamura, M. Synthesis of BN-Fused Polycyclic Aromatics via Tandem Intramolecular Electrophilic Arene Borylation. J. Am. Chem. Soc. 2011, 133 (46), 18614-18617. (b) Hatakeyama, T.; Hashimoto, S.; Oba, T.; Nakamura, M. Azaboradibenzo [6] helicene: Carrier Inversion Induced by Helical Homochirality. J. Am. Chem. Soc. 2012, 134 (48), 19600-19603. (c) Wang, X.-Y.; Lin, H.-R.; Lei, T.; Yang, D.-C.; Zhuang, F.-D.; Wang, J.-Y.; Yuan, S.-C.; Pei, J. Azaborine Compounds for Organic Field-Effect Transistors: Efficient Synthesis, Remarkable Stability, and BN Dipole Interactions. Angew. Chem., Int. Ed. 2013, 52 (11), 3117-3120. (d) Miyamoto, F.; Nakatsuka, S.; Yamada, K.; Nakayama, K.-i.; Hatakeyama, T. Synthesis of Boron-Doped Polycyclic Aromatic Hydrocarbons by Tandem Intramolecular Electrophilic Arene Borylation. Org. Lett. 2015, 17 (24), 6158-6161. (e) Katayama, T.; Nakatsuka, S.; Hirai, H.; Yasuda, N.; Kumar, J.; Kawai, T.; Hatakeyama, T. Two-Step Synthesis of Boron-Fused Double Helicenes. J. Am. Chem. Soc. 2016, 138 (16), 5210-5213.

(16) (a) Feng, J.; Tian, K.; Hu, D.; Wang, S.; Li, S.; Zeng, Y.; Li, Y.; Yang, G. A Triarylboron-Based Fluorescent Thermometer: Sensitive Over a Wide Temperature Range. Angew. Chem., Int. Ed. 2011, 50 (35), 8072-8076. (b) Neena, K. K.; Sudhakar, P.; Dipak, K.; Thilagar, P. Diarylboryl-phenothiazine based multifunctional molecular siblings. Chem. Commun. 2017, 53 (26), 3641-3644. (c) Li, S.-Y.; Hui, Y.-J.; Sun, Z.-B.; Zhao, C.-H. A triarylborane-based biphenyl exhibiting abrupt fluorescence enhancement at a specific high temperature. Chem. Commun. 2017, 53 (24), 3446-3449. (d) Shi, Y.-g.; Wang, J.-w.; Li, H.; Hu, G.-f.; Li, X.; Mellerup, S. K.; Wang, N.; Peng, T.; Wang, S. A simple multi-responsive system based on aldehyde functionalized amino-boranes. Chem. Sci. 2018, 9 (7), 1902-1911. (e) Sun, Z.-B.; Liu, J.-K.; Yuan, D.-F.; Zhao, Z.-H.; Zhu, X.-Z.; Liu, D.-H.; Peng, Q.; Zhao, C.-H. 2,2'-Diamino-6,6'-diboryl-1,1'-binaphthyl: A Versatile Building Block for Temperature-Dependent Dual Fluorescence and Switchable Circularly Polarized Luminescence. Angew. Chem., Int. Ed. 2019, 58 (15), 4840-4846.

(17) (a) Huh, J. O.; Do, Y.; Lee, M. H. A BODIPY–Borane Dyad for the Selective Complexation of Cyanide Ion. *Organometallics* **2008**, 27 (6), 1022–1025. (b) Yamaguchi, S.; Akiyama, S.; Tamao, K. Colorimetric Fluoride Ion Sensing by Boron-Containing π -Electron Systems. J. Am. Chem. Soc. **2001**, 123 (46), 11372–11375. (c) Wade, C. R.; Gabbaï, F. P. Cyanide and Azide Anion Complexation by a Bidentate Stibonium-Borane Lewis Acid. Z. Naturforsch., B: J. Chem. Sci. 2014, 69b, 1199–1205. (d) Yin, X.; Liu, K.; Ren, Y.; Lalancette, R. A.; Loo, Y.-L.; Jäkle, F. Pyridalthiadiazole acceptor-functionalized triarylboranes with multi-responsive optoelectronic characteristics. Chem. Sci. 2017, 8 (8), 5497–5505. (e) Sudhakar, P.; Neena, K. K.; Thilagar, P. Borylated perylenediimide: self-assembly, photophysics and sensing application. Dalton Trans. 2019, 48 (21), 7218–7226. (f) Teerasarunyanon, R.; Wilkins, L. C.; Park, G.; Gabbaï, F. P. Synthesis, structure and anion binding properties of 1,8-bis-(dimesitylboryl)anthracene and its monoborylated analog. Dalton Trans. 2019, 48 (39), 14777–14782.

(18) (a) Pagidi, S.; Kalluvettukuzhy, N. K.; Thilagar, P. Triarylboron Anchored Luminescent Probes: Selective Detection and Imaging of Thiophenols in the Intracellular Environment. *Langmuir* **2018**, 34 (28), 8170–8177. (b) Griesbeck, S.; Michail, E.; Wang, C.; Ogasawara, H.; Lorenzen, S.; Gerstner, L.; Zang, T.; Nitsch, J.; Sato, Y.; Bertermann, R.; Taki, M.; Lambert, C.; Yamaguchi, S.; Marder, T. B. Tuning the π -bridge of quadrupolar triarylborane chromophores for one- and two-photon excited fluorescence imaging of lysosomes in live cells. *Chem. Sci.* **2019**, *10* (20), 5405–5422. (c) Griesbeck, S.; Ferger, M.; Czernetzi, C.; Wang, C.; Bertermann, R.; Friedrich, A.; Haehnel, M.; Sieh, D.; Taki, M.; Yamaguchi, S.; Marder, T. B. Optimization of Aqueous Stability versus π -Conjugation in Tetracationic Bis(triarylborane) Chromophores: Applications in Live-Cell Fluorescence Imaging. *Chem. - Eur. J.* **2019**, *25* (32), 7679–7688.

(19) Yamaguchi, S.; Shirasaka, T.; Tamao, K. Tridurylboranes Extended by Three Arylethynyl Groups as a New Family of Boron-Based π -Electron Systems. Org. Lett. **2000**, 2 (26), 4129–4132.

(20) Stahl, R.; Lambert, C.; Kaiser, C.; Wortmann, R.; Jakober, R. Electrochemistry and Photophysics of Donor-Substituted Triarylboranes: Symmetry Breaking in Ground and Excited State. *Chem. - Eur. J.* **2006**, *12* (8), 2358–2370.

(21) Liu, Y.; Xie, G.; Wu, K.; Luo, Z.; Zhou, T.; Zeng, X.; Yu, J.; Gong, S.; Yang, C. Boosting reverse intersystem crossing by increasing donors in triarylboron/phenoxazine hybrids: TADF emitters for high-performance solution-processed OLEDs. *J. Mater. Chem. C* **2016**, *4* (20), 4402–4407.

(22) (a) Sudhakar, P. Rational design and facile synthesis of boryl anilines: intriguing aggregation induced emission and external stimuli responsive properties. Ph.D. Dissertation, Indian Institute of Science, Bangalore, India, 2015. (b) Sudhakar, P.; Neena, K. K.; Thilagar, P. H-Bond assisted mechanoluminescence of borylated aryl amines: tunable emission and polymorphism. *J. Mater. Chem. C* 2017, *S*, 6537–6546.

(23) Yoshino, J.; Nakamura, Y.; Kunitomo, S.; Hayashi, N.; Higuchi, H. Synthesis of tris(4-amino-2,6-dimethylphenyl)borane and facile extension of its π -conjugated system by utilizing the reactivity of the amino groups. *Tetrahedron Lett.* **2013**, *54* (22), 2817–2820.

(24) Mao, M.; Ren, M.-G.; Song, Q.-H. Thermodynamics and Conformations in the Formation of Excited States and Their Interconversions for Twisted Donor-Substituted Tridurylboranes. *Chem. - Eur. J.* 2012, *18* (48), 15512–15522.

(25) Zoon, P. D.; Brouwer, A. M. A push-pull aromatic chromophore with a touch of merocyanine. *Photochem. Photobiol. Sci.* **2009**, *8* (3), 345–353.

(26) Zhang, Z.; Edkins, R. M.; Nitsch, J.; Fucke, K.; Steffen, A.; Longobardi, L. E.; Stephan, D. W.; Lambert, C.; Marder, T. B. Optical and electronic properties of air-stable organoboron compounds with strongly electron-accepting bis(fluoromesityl)boryl groups. *Chem. Sci.* **2015**, *6* (1), 308–321.

(27) Kushida, T.; Camacho, C.; Shuto, A.; Irle, S.; Muramatsu, M.; Katayama, T.; Ito, S.; Nagasawa, Y.; Miyasaka, H.; Sakuda, E.; Kitamura, N.; Zhou, Z.; Wakamiya, A.; Yamaguchi, S. Constraint-induced structural deformation of planarized triphenylboranes in the excited state. *Chem. Sci.* **2014**, *5* (4), 1296–1304.

(28) Januszewski, E.; Lorbach, A.; Grewal, R.; Bolte, M.; Bats, J. W.; Lerner, H.-W.; Wagner, M. Unsymmetrically Substituted 9,10Dihydro-9,10-diboraanthracenes as Versatile Building Blocks for Boron-Doped π -Conjugated Systems. *Chem. - Eur. J.* **2011**, 17 (45), 12696–12705.

(29) Jia, W.-L.; Song, D.; Wang, S. Blue Luminescent Three-Coordinate Organoboron Compounds with a 2,2'-Dipyridylamino Functional Group. *J. Org. Chem.* **2003**, *68* (3), 701–705.

(30) Venkatasubbaiah, K.; Pakkirisamy, T.; Lalancette, R. A.; Jäkle, F. Tuning the electronic structure of diboradiferrocenes. *Dalton Trans.* **2008**, No. 33, 4507–4513.

(31) Dobek, K.; Karolczak, J. The Influence of Temperature on C153 Steady-State Absorption and Fluorescence Kinetics in Hydrogen Bonding Solvents. J. Fluoresc. **2012**, *22* (6), 1647–1657.

(32) (a) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98 (7), 5648-5652. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, O.; Farkas, A. D.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009. (c) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. A: At., Mol., Opt. Phys. 1988, 38 (6), 3098-3100. (d) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B: Condens. Matter Mater. Phys. 1988, 37 (2), 785-789.